

Electrochemical and Surface Imaging Studies of the Initiation and Rapid Termination of the Growth of Localized Corrosion Sites on Carbon Steel Microelectrodes.

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BACKGROUND

Control of localized corrosion such as pitting [1] and crevice corrosion can be very challenging. The need to use costly preventative measures such as corrosion inhibitors is dependent on the ability to detect whether localized corrosion is taking place. When it occurs in locations that are very difficult, or impossible, to observe, remote monitoring of the onset of localized corrosion is of particular interest.

Our group is interested in developing carbon steel microelectrodes as a means of probing and perhaps monitoring such behavior on high grade carbon steel under conditions that favor localized corrosion [2]. The advantage of such electrodes is that they show an immediate and readily identifiable response when localized corrosion occurs. The downside is that, because of their small size (on the order of tens to hundreds of microns in diameter), their electrochemical response changes as their surfaces become rapidly altered. To minimize this problem, applied potential biases and rapid changes in inhibitor concentrations were employed to control the surface damage. The latter approach is also particularly useful as a direct test of an inhibitor's effectiveness in stopping localized corrosion.

EXPERIMENTAL METHOD & RESULTS

In this study, we employed an aerated nitrite solution as the inhibitor system, and varying concentrations of chloride as the aggressor ion. This system was chosen, in part, because carbon steel surfaces tend to be highly passive in nitrite solutions, even in the presence of adventitious oxygen associated with our *in situ* atomic force microscopy (AFM) studies [2-4]. By varying the applied bias potential and the ratio of chloride to nitrite, the timing for the initiation and termination of localized corrosion can be controlled to a greater degree.

Experiments consisted of oxidizing well characterized (via AFM and SEM), 30 to 300 μm dia. carbon steel disk electrodes using a standard 3-electrode setup. Solutions ranged from 0.025 to 0.1 M NaNO_2 , and included ratios of 1:1 and 3:1 chloride (NaCl) to nitrite. The majority of the experiments employed a zero resistance ammeter (ZRA) while driving the potential of the microelectrode anodic relative to the counter electrode. When needed, a simple flow-cell (flow rates set at 1 to 3 ml/min) was used to rapidly change the solution conditions from passive to aggressive, and *vice versa*.

Under anodically biased potentials, active, localized corrosion can be readily induced in a solution containing 3:1 chloride to nitrite. Once started, this corrosion is stopped by going to the open circuit potential (OCP), which typically is negative of the repassivation potential. In the example given in figure 1, subsequent application of a far less oxidizing potential of 0.3 V (relative to the counter electrode, or ca. 0.31

V relative to a $\text{Fe/sat.FeCO}_3/0.5\text{MNaHCO}_3$ reference electrode) tended to reinitiate localized corrosion after an induction period. As seen in figure 1, the duration and magnitude of potential biases closer to OCP (defined as a 0 V bias) directly determined how fast, and to what magnitude, localized corrosion currents would reinitiate at the 0.3 V bias. In figure 2, it can be seen that changing the solution conditions from aggressive to more passive can also rapidly affect the localized corrosion currents. In general, it was observed that controlling the initiation and termination of localized corrosion, although highly variable, followed expected trends in that more negative applied potentials and more passivating solutions terminated active corrosion and restricted reinitiation. This presentation will address the trends observed as a function of surface damage with time and duration of applied potential bias.

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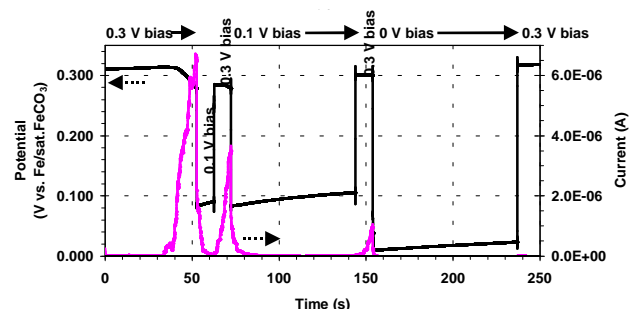


Figure 1. Variable voltage biased ZRA study of a $\sim 25 \times 40 \mu\text{m}$ carbon steel electrode in 0.02 M $\text{NaNO}_2/0.06 \text{ M NaCl/air}$. The large current spikes correspond to active, localized corrosion. Note that immediately prior to this experiment the electrode was subjected to a 10 mV/s ramped potential experiment, in the same solution, where sustained localized corrosion initiated at ca. 0.72 V and showed repassivation at 0.08 V vs Fe/sat.FeCO_3 .

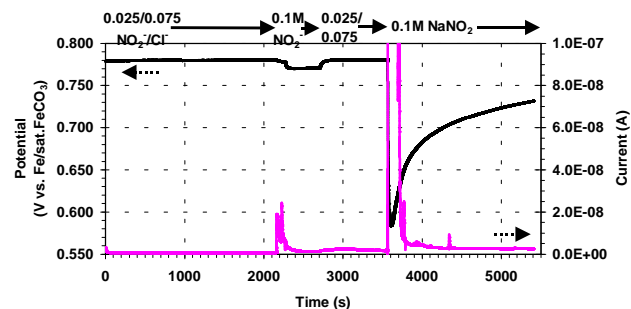


Figure 2. 0.6 V biased ZRA study of a $\sim 8 \times 40 \mu\text{m}$ carbon steel electrode in a flow cell (2 ml/min) as the solution is varied between 0.1 M NaNO_2 and 0.025 M $\text{NaNO}_2/0.075 \text{ M NaCl/air}$. The large current spikes correspond to active, localized corrosion.